Notes: Chapter 19

Wednesday, January 10, 2007
12:02 AM

Chapter 19
Ionic Equilibria in Aqueous Systems

Homework:

Buffers

By definition a buffer resists the change in the pH when small amounts of either acid or base are added to the solution. A buffer is an acid-conjugate base or base-conjugate acid chemical system. In the human body buffers are at work constantly to maintain a blood pH of between 6.8 and 7.8. Outside this range life is not possible.

How Buffers Work: The Common Ion Effect

When a weak acid is mixed with its conjugate base the pH is moderated some where between the pH expected of either the acid alone or conjugate base alone. Likewise, when a weak base is mixed with its conjugate acid the pH is moderated some where between the pH expected of either the base alone or conjugate acid alone.

This causes a buffering effect that resists a change in the pH. This buffering effect is because both acid and conjugate base are present in the solution. When strong acid is added to the solution, the base reacts with it producing a weak acid. When strong base is added to the solution, the acid reacts with it producing a weak base.

There are several ways to get an acid and conjugate base, or base and conjugate acid in a solution at the same time. One could put a weak acid or base and a salt containing its conjugate in the solution thus creating a buffer, or one could put a weak acid with a strong base, or one could put a weak base with a strong acid. No matter how the solution is created;

1. All equilibria must be obeyed simultaneously.
2. The stronger acid or base controls the pH.
3. Excess strong acid or base controls the pH.
4. The final concentrations of species are what control the pH.

Problem:

a) Design a buffer system having a pH of 3 using acetic acid and sodium acetate.

b) Calculate the pH for a liter of water to which 1 mL of 1M HCl has been added.

c) Calculate the pH for a liter of water to which 1 mL of 1M NaOH has been added.

d) Calculate the pH for a liter of the buffer system created in part a) when 1 mL of 1M HCl has been added.

e) Calculate the pH for a liter of the buffer system created in part a) when 1 mL of 1M NaOH has been added.

Problem:

Design a buffer having a pH of 8.2.

Problem:

Find the pH of a solution made by adding 30 ml of .5 M HCl to 50 ml of 1 M NH_4.

Problem:

Find the pH of a solution made by adding .1 moles of HCN and .05 moles of KCN to 100 ml of water.

Titrations and pH Curves

Problem: Strong acid-strong base titration

Accurately draw a titration curve for the addition of .1 M NaOH into 10 mL of .1 M HCl. Use 1 mL increments and add a total of 15 mL of base.

Liters			Total	Total	xs mol	xs mol			
V_{base}	V_{acid}	V_{total}	mol H^+	mol OH^-	H^+	OH^-	$[H^+]$	$[OH^-]$	pH
0	.010	.010	.001	0	.01	0	.1	$1 x 10^{-13}$	1
.001	.010	.011	.001	.0001	.0009	0	.08182	$1.22 x 10^{-13}$	1.09
.002	.010	.012	.001	.0002	.0008	0	.06667		
.003	.010	.013							
.004	etc….								

Use a spreadsheet to finish filling out all data up to 15mL of base added and draw an accurate pH vs mL base graph.

Problems to consider for your graph.

a) On your graphs clearly show the equivalence point.

b) Find the pH at 5 ml. (The half equivalence point) This should be no surprise.

c) What indicator(s) should be used for the neutralization of this strong acid.

d) Is there any buffering effect for the titration of a strong acid-strong base titration?

Problem: Weak acid-strong base titration

Accurately draw a titration curve for the addition of .1 M NaOH into 10 mL of .1 M HOAc. K_a=1.8x10^{-5}. Use 1 mL increments and add a total of 15 mL of base.

Liters			Mole	Mole	xs mole	mole			xs mol			
V(base)	V(acid)	V(total)	HOAc	OH	HOAc	OAc-	[HOAc]	[OAc-]	OH-	[H+]	[OH-]	pH
0	0.01	0.01	0.001	0	0.001	0	0.1	1.34E-03	0	1.34E-03	7.44E-12	2.87
0.001	0.01	0.011	0.001	0.0001	0.0009	0.0001	0.081818	0.009091	0	1.62E-04	6.17E-11	3.79
0.002	0.01	0.012	0.001	0.0002	0.0008	0.0002	0.066667	0.016667	0	7.20E-05	1.39E-10	4.14
0.003	0.01	0.013										
0.004	0.01	0.014										
0.005												
0.006												
0.007												
etc...												

Use a spreadsheet to finish filling out all data up to 15mL of base added and draw an accurate pH vs mL base graph.

Problems to consider for your graph.

a) On your graph clearly show the equivalence point. What is the pH at the equivalence point.

b) Find the pH at 5 ml. Clearly mark the half equivalents point on the graph.

c) Find the [H^+] at the half equivalents point. Does this look familiar?
d) Prove that K_a=[H^+] at the half equivalents point.
e) What indicators should be used for a neutralization titration for this acid.
f) Clearly indicate the buffer region on the graph.

The Henderson-Hasselbalch Equation
pH=pK_a + log([base]/[acid])

Problem:
Use the Henderson-Hasselbalch equation to calculate the pH at the one fourth equivalents point for your acetic acid - sodium hydroxide graph; i.e. 2.5 mL NaOH added.

Solubility Product Constant (K_{sp})

When a salt dissolves in water the ions dissociate and are present in solution in the same proportions found in the salt.

$C_xA_{y(s)}$ ---> $xC_{(aq)}$ + $yA_{(aq)}$

Note: C=cation, A=anions, and x & y are the subscripts for the salt.
When a salt is saturated or the salt is only slightly soluble in water, an equilibrium is set up between the solid and aqueous phases of the salt.

$C_xA_{y(s)}$ <===> $xC_{(aq)}$ + $yA_{(aq)}$

The equilibrium expression for this process is:

K_{eq} = $[C_{(aq)}]^x[A_{(aq)}]^y/[C_xA_{y(s)}]$

The concentration of the solid phase has no physical meaning and is assigned a constant value of 1. This leads to the general expression for the solubility product:

Q_{sp} = $[Cations]^x[Anions]^y$ **which equals K_{sp} at saturation.**

If $[Cations]^x[Anions]^y < K_{sp}$ the solution is unsaturated and can dissolve more solid. If $[Cations]^x[Anions]^y = K_{sp}$ the solution is saturated and no more solid can dissolve. If $[Cations]^x[Anions]^y > K_{sp}$ the solution is supersaturated and precipitation will occur until saturation is reached.

Problem:
Write the K_{sp} expressions for AgCl and Ag_2CrO_4. Which salt AgCl or Ag_2CrO_4 will form a more concentrated saturated solution? $K_{sp(AgCl)}=1.8\times10^{-10}$, $K_{sp(Ag2CrO4)}=1.1\times10^{-12}$

Problem:
a) How many grams of $PbCl_2$ can dissolve in 100 g of water? $K_{sp}=1.6\times10^{-5}$.
b) What must the chloride concentration be brought to in order to reduce the [Pb^{2+}] to half the saturation level.

Problem:
A solution is .2 M $Pb(NO_3)_2$. How many grams of NaCl need to be added to this solution to lower the Pb^{2+} concentration to .001 M?

Problem:
What is the maximum concentration of chloride that can exist in a .1 M $AgNO_3$ solution and not cause any precipitation?

Problem:
What concentration of sulfide must be present to make a maximum separation of zinc ions and copper ions? Assume that both concentrations are .1 M initially. $K_{sp(ZnS)}=1.1\times10^{-21}$, $K_{sp(CuS)}= 6\times10^{-36}$

Problem:
What percent of copper ions was removed in the above problem?

Problem:
$H_2S_{(g)}$ is soluble in water to the extent of .1 M at 1 atm. What must the pH be in order to make the maximum separation of zinc ions and copper ions? Assume that both concentrations are .1 M initially. $K_{a1}K_{a2}=K_{aH2S}= 1.1\times10^{-20}$

Effect of pH on Solubility

For many reactions, the equilibrium will be shifted by the addition of either acid or base. The H^+ or OH^- may react directly with one of the ionic species of the salt or may set up another equilibrium, which increases or decreases the concentration of one of the ionic species. Here are examples of each.

Problem:
At what pH will a solution of .1 M $AlCl_3$ give precipitation? $K_{sp} = 4.6\times10^{-33}$

Problem:
CaC_2O_4 is relatively insoluble in neutral and basic solutions; however in acidic solutions it becomes much more soluble. Determine the solubility of CaC_2O_4 in 1 liter of water when the pH has been adjusted to 7 and then adjusted to 2.
$K_{sp}=2.3\times10^{-9}$, $K_{a1}K_{a2}=K_{aH2C2O4}=2.86\times10^{-6}$

From this example, you can see that all equilibria must be simultaneously satisfied.

Complex-Ion Equilibria

A complex ion is an ion formed by attaching electron pair donors called ligands to metal ions. A brief list of ligands: NH_3, CN^-, OH^-, Cl^-, H_2O, Cl^-. One thing that all ligands have is common is *a pair of electrons to donate the central ion.*

We treat complex-ion equilibria just like any other equilibrium; however, we may think of the equilibria as either formation of complex ions or the dissociation of complex ions. Consider the formation of silver ammine complex:

Ag^+ +2NH_3 ---> $Ag(NH_3)_2^+$ $K_{formation}$= $[Ag(NH_3)_2^+]/[Ag^+][NH_3]^2$

Consider the dissociation of the silver ammine complex:

$Ag(NH_3)_2^+$ --- Ag^+ +2NH_3 $K_{dissociation}$= $[Ag^+][NH_3]^2/[Ag(NH_3)_2^+]=\frac{1}{K_f}$

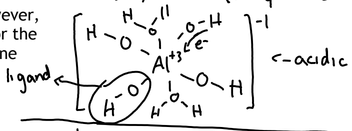
Problem:
.1 moles of $AgNO_3$ is dissolved in 100 mL of 6M NH_3. What is the [Ag^+]?

Problem:
At what pH will 1 mole of $Zn(OH)_2$ completely dissolve in 1 L to form the $Zn(OH)_4^{-2}$ complex?

It is a general rule that all equilibria must be obeyed

$Al^{+3} + 3OH^- \rightarrow Al(OH)_{3(s)}$

$Al(OH_3)_{(s)} + OH^- \rightarrow Al(OH)_4^- \cdot 2H_2O$



complex ions

$Fe(SCN)^{+2}$ $Ag(NH_3)_2^+$

assume 1L

$K_f\ Ag(NH_3)_2 = 1.7\times10^7$

$$\begin{array}{lccc} & 1M & 6M & 0 \\ & Ag^+ + & 2NH_3 \rightleftharpoons & Ag(NH_3)_2^+ \\ \text{if 100\% to RT: F} & 0 & 4 & 1 \\ \text{c} & & & \\ \text{Reverse reaction F} & x & 4+2x & 1-x \end{array}$$

$$\begin{array}{lcccc} \text{I} & 2 & 6 & 0 & 0 \\ \text{F} & AgCl(s) & +2NH_3 \rightarrow & Ag(NH_3)_2^+ & +Cl^- \end{array}$$

$$1.7\times10 = \frac{(1-x)}{(x)(4+2x)^2}$$

$[Ag^+] = x = 3.67\times10^{-9}$

assume 1L

$$\begin{array}{lcccc} I & 1 & 2 & & 0 \\ & Zn(OH)_{2(s)} & +\,2OH^- & \rightarrow & Zn(OH)_4^{-2} \\ = & 0 & & & 1 \end{array}$$

$$K_{eq} = \frac{[Zn(OH)_4^{-2}]}{[OH]^2}$$

K_f $Zn(OH)_4^{-2} = \frac{[Zn(OH)_4^{-2}]}{[Zn^{+2}][OH^-]^4}$ $Zn^{+2} + 4OH^- \rightleftharpoons Zn(OH)_4^{-2}$

$K_{sp} = [Zn^{+2}][OH^-]^2$ $Zn(OH)_{2(s)} \rightleftharpoons Zn^{+2} + 2OH^-$

$K_f \cdot K_{sp} = K_{eq}$

$$\frac{[Zn(OH)_4^{-2}]}{[Zn^{+2}][OH^-]^4} \times [Zn^{+2}][OH^-]^2 = \frac{[Zn(OH)_4^{-2}]}{[OH^-]^2}$$

$K_f = 3\times10^{15}$ $K_{sp} = 3\times10^{-16}$

$K_{eq} = .9$

$$[OH^-] = \sqrt{\frac{1}{.9}} = 1.054$$

$pOH = -.0228$

$pH = 14.02$

simultaneously. Consider the interplay between the complex-ion equilibria and solubility equilibria for the insoluble salt, AgCl, and the stable complex, $Ag(NH_3)^+$:

Problem:

Will .2 moles of AgCl dissolves in 100 ml of 6M NH_3?

$K_{sp} \cdot K_f = K_{eq} = 1.8\times10^{-10} \cdot 1.7\times10^7 = .00306$

$$K_{eq} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = \frac{2\cdot2}{2^2} = 1 = Q$$

$Q > K \rightarrow$ No

Problem:

Calculate the maximum amount of AgCl that can dissolve in 100 mL of 6 M NH_3.

$$\begin{array}{ccccccc} x & & 6 & & 0 & & 0 \\ AgCl(s) & + & 2NH_3 & \rightarrow & Ag(NH_3)_2 & + & Cl^- \\ 0 & & 6-2x & & x & & x \end{array}$$

$$.00306 = \frac{x^2}{(6-2x)^2}$$

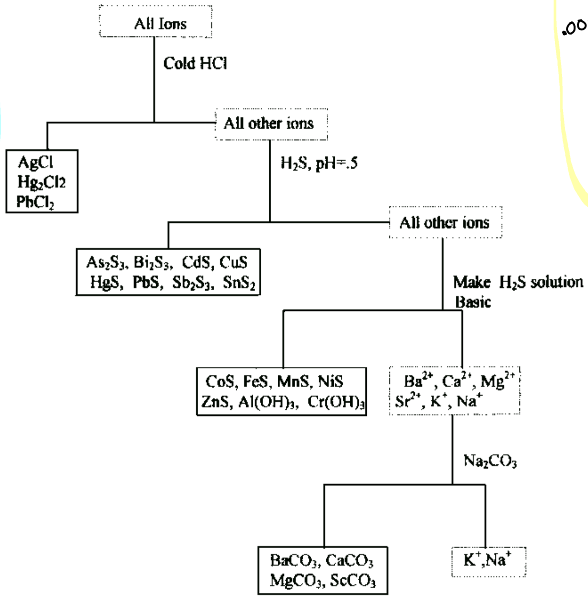
$6\sqrt{3.06\times10^{-3}} + 2\sqrt{3.06\times10^{-3}}\,x = x$

$x = .299$

x = amt AgCl (s) dissolved in 1L

in 100 mL = .0299 mole

Application of Solubility Equilibria in Qualitative Chemical Analysis



Pasted from <http://fp.academic.venturacollege.edu/doliver/chem1b/notes/Chap19new.htm>

(114) KCl 3.7 M @ 20°C 100 mL

100 mL 6M HCl

100 mL 12M HCl

$K_{sp} = [K^+][Cl^-] = (3.7M)(3.7M) = 13.69$

$$13.69 \overset{?}{=} \left(\frac{3.7}{2}\right)\left(\frac{.37\,mol + .6\,mol}{.2L}\right) = Q = 8.97$$

Q<K no precipitate

$$13.69 \overset{?}{=} \left(\frac{.37\,mol}{.2L}\right)\left(\frac{.37+1.2}{.2L}\right) = 14.5$$

Q>K

How much precipitates?

$K_{sp} = [K^+][Cl^-]$

$$13.69 = \left(\frac{.37}{.2}\right)(x)$$

$x = 7.4\ M\ Cl^-$ <– total that can dissolve

$$\begin{array}{ccccc} 1.85 & & 7.85 & & \\ K^+ & + & Cl^- & \rightarrow & KCl \\ 1.85-x & & 7.85-x & & x \end{array}$$

$13.69 = (1.85-x)(7.85-x)$

$0 = x^2 - 9.7x + .8325$

$$x = \frac{9.7 \pm \sqrt{9.7^2 - 4(.8325)}}{2}$$

$x = 0.088697M$

$$\frac{.0088697\,mol}{1L} \times .200L \times \frac{74.55g\,KCl}{1\,mol} = \boxed{1g}$$